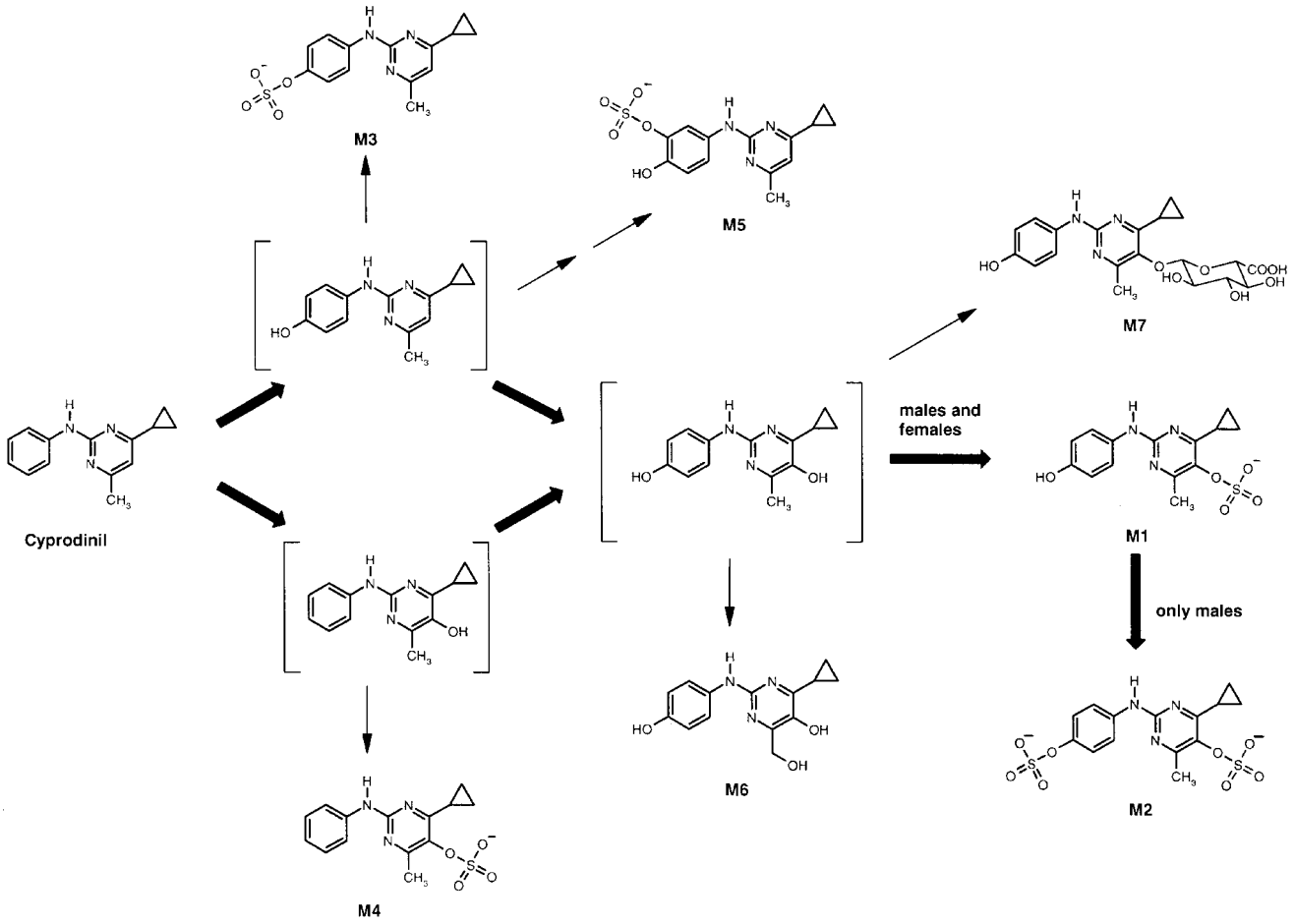

Figure 2. Major metabolic pathways of cyprodinil in the rat.

ase is sex-dependent, since only male rats formed the disulfate conjugate. Sex-related differences have been reported for the activity of some phenol sulfotransferases in rat liver.[9] For instance, large amounts of phenol sulfotransferase 1 were found for both sexes while large amounts of phenol sulfotransferase 2 were restricted to males.[10] However, it remains to be determined which sex-specific sulfotransferase is involved in the formation of the disulfate conjugate M2.

5 CONCLUSION

Cyprodinil is rapidly excreted, principally in the urine, after a single oral administration. Excretion of the administered dose is independent of the dose level and the sex. The major Phase I metabolites are conjugated with sulfate. Only male rats form a disulfate conjugate, suggesting a sex dimorphism in the activity of a specific sulfotransferase that catalyzes the transfer of the second sulfate group.

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The microbial biodegradation of paraquat in soil

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Abstract: The microbial degradation of [^{14}C]paraquat using cultures from two agricultural soils was investigated. The experiments were carried out in the absence of light, under aerobic conditions.

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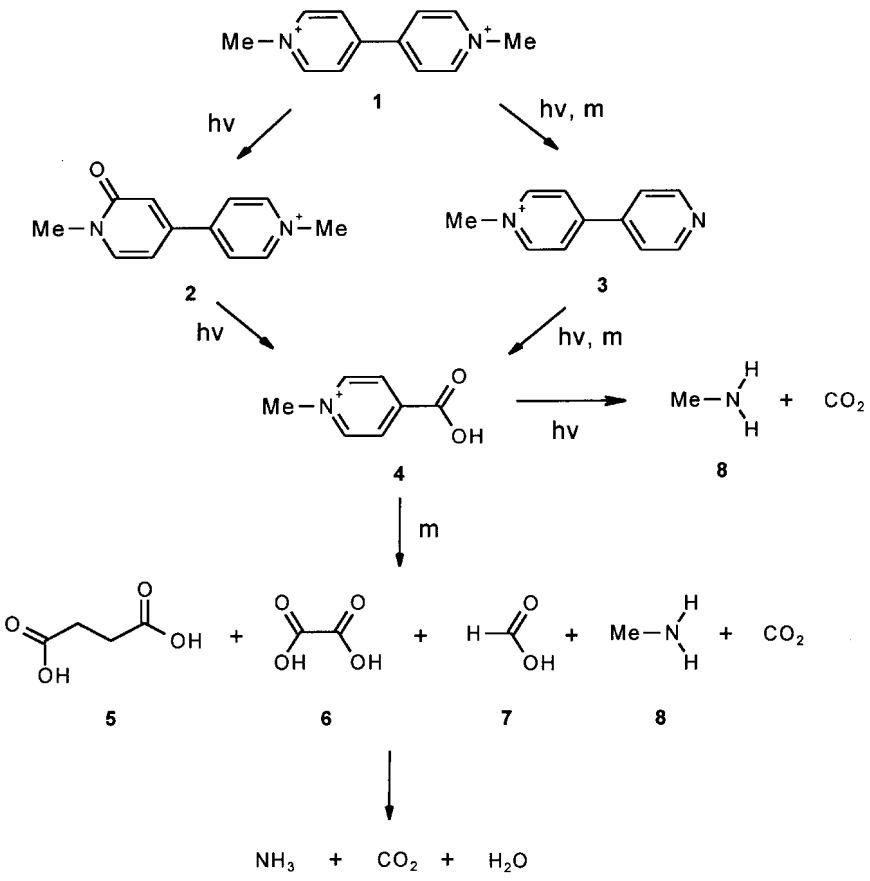

Figure 1. Scheme for the biodegradation of paraquat on and in soil. m = micro-organism cultures; hv = sunlight (paraquat on soil) or UV light (paraquat in solution).

Degradation was rapid, with 50% mineralisation to [^{14}C]carbon dioxide occurring within three weeks. HPLC, capillary electrophoresis and mass spectroscopy confirmed that the majority (>85%) of the remaining radiochemical in solution was [^{14}C]oxalic acid, and that no paraquat remained.

Keywords: paraquat; biodegradation; soil solution; mineralisation

1 INTRODUCTION

The contact herbicide paraquat (Fig 1; **1**) is used to control weeds in a wide range of crops. Once paraquat enters the soil environment it is rapidly and strongly bound to clay minerals and organic matter and deactivated.[1]

Several studies have used pure cultures of soil micro-organisms to elucidate the degradative pathways of ring-labelled paraquat, (Fig 1).[2–6] These studies established the range of bacteria and fungi capable of degrading paraquat (eg *Corynebacterium fascians* Dows, *Lipomyces starkeyi* Loo & Rij, *Aspergillus niger* van Teigh, *Penicillium frequentans* West, *Fusarium* sp and *Pseudomonas* sp) and that conditions in soil solution are conducive to the degradation of paraquat.

The purpose of the current study was to determine if micro-organisms cultured from soil would rapidly and extensively degrade bioavailable paraquat.

2 EXPERIMENTAL

[^{14}C]Paraquat (10 or 100 mg litre^{-1}) was added to incubation vessels containing cultures extracted from two UK sandy loam soils (Frensham, OS Ref SU 834397, 1.2% organic matter, pH 5.9 and Broadricks, OS Ref SU 873727, 2.1% organic matter, pH 5.8). The paraquat/soil test mixtures were incubated at 20 °C, in the absence of light and under aerobic conditions in mineral salts medium (50 or 100 ml) for between 20 and 36 days with regular sampling for volatile products.

The mineral salts medium (pH 6.8) comprised potassium hydrogen phosphate, (1.0); potassium chloride (0.5); magnesium sulphate heptahydrate (0.5); iron sulphate heptahydrate (0.02); sodium hydrogen phosphate (0.37) and sodium dihydrogen phosphate, (0.33 g litre^{-1}). Each test application vessel also contained sucrose (10 g litre^{-1}) as a carbon source to aid microbial growth.

The soils (20 replicates) were sampled using a 30 × 2.5 cm auger corer, mixed and sieved to a particle size of ≤2 mm before storage at 5 °C until use. The soil was sonicated in water (1 g in 10 ml) and inoculated with the appropriate subculture (10 µl) in mineral salts medium then incubated for 1 week; three conseculture experiments per sample were run. All experiments were carried out under aerobic conditions, in a constant temperature room (20 °C), in the absence of light.

The non-volatile metabolites remaining in solution were isolated by centrifugation, acidification (pH 2) and extraction into ethyl acetate (3 × 50 ml) and analysed by high performance liquid chromato-

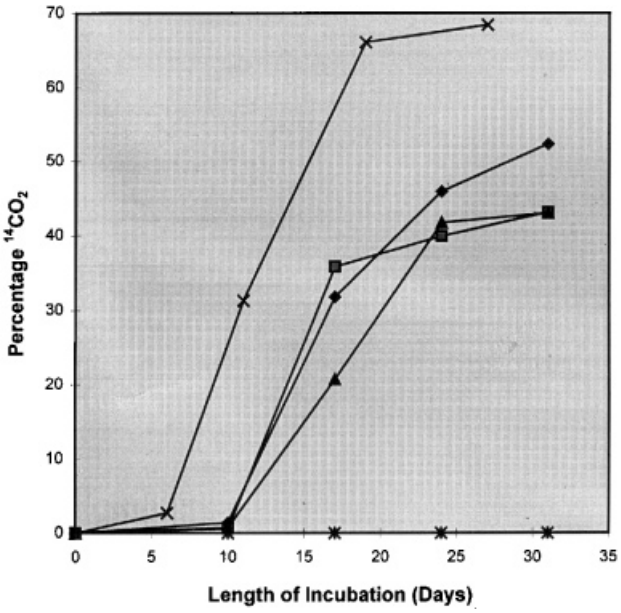

Figure 2. Typical mineralisation plots; cumulative [^{14}C] carbon dioxide, 10 mg litre^{-1} application. × incubation 1, ◆ incubation 2, ■ incubation 3, ▲ incubation 4, ∗ control.

graphy, capillary electrophoresis and mass spectrometry.

The test chemical, [*ring-U*-^{14}C]paraquat (specific activity, 2.0 GBq mmol^{-1}) was supplied by the Jealott's Hill radiochemistry department. The radiochemical was diluted with non-radiolabelled paraquat (99.7% pure) prior to use.

3 RESULTS

Paraquat was extensively metabolised with the rapid production of [^{14}C]carbon dioxide. Typical mineralisation (to CO_2) values were around 50% for both soil extracts and typical [^{14}C]carbon dioxide evolution plots are shown in Fig 2.

Chromatographic analysis of the residual radiochemical in solution at the end of each incubation showed almost identical metabolite profiles between the different micro-organisms. A major metabolite, comprising >85% of the radioactivity remaining in the incubated solution, together with a minor metabolite (<5%), and a metabolite which was incorporated into the degrading microbial cultures (<10%), were characterised. The major metabolite was identified as oxalic acid (**6**), and no paraquat remained in the solutions.

4 DISCUSSION AND CONCLUSIONS

This work has shown that bioavailable paraquat can be rapidly and completely degraded by micro-organisms present in soil. Complete degradation of paraquat takes less than two or three weeks, indicating that the half-life of bioavailable paraquat is considerably shorter than this. The metabolism was so fast that only small fragments of naturally occurring acids, and carbon dioxide as the ultimate mineralisation product, were seen.

These laboratory results correlate well with long-term field trial data, taking into consideration the bioavailability of paraquat in the soil environment.[7]

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Factors controlling degradation of pesticides in soil

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Abstract: Rates of pesticide degradation in soil exhibit a high degree of variability, the sources of which are usually unclear. Combining data from incubations performed using a range of soil properties and environmental conditions has resulted in greater understanding of factors controlling such degradation. The herbicides clomazone, flumetsulam, atrazine, and cloransulam-methyl, as well as the former insecticide naphthalene offer examples of degradation kinetics controlled by coupling competing processes which may in turn be regulated separately by environmental conditions and soil properties. The processes of degradation and volatilization appear to compete for clomazone in solution; sorbed clomazone is degraded only after the solution phase is depleted. Similarly, volatilization of naphthalene is enhanced when degradation has been inhibited by high nutrient levels. Degradation of the herbicide flumetsulam has been shown to be regulated by sorption, even though the compound has a relatively low affinity for the soil. The fate pathway for cloransulam-methyl shifts from mineralization to formation of metabolities, bound residues and physically occluded material as temperature increases. Atrazine degradation in soil may be controlled in part by the presence of inorganic nitrogen, as the herbicide appears to be used as a nitrogen source by micro-organisms. New insight

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